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METAL TRANSPORT AND RETENTION: THE ROLE OF DISSOLVED ORGANIC CARBON

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METAL TRANSPORT AND RETENTION:

THE ROLE OF DISSOLVED ORGANIC CARBON

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ABSTRACT

In the dilute Precambrian Shield waters of Canada, Pb, Cu, Fe and Hg concentrations are correlated with Dissolved Organic Carbon (DOC). These metals are exported from both upland and wetland organic soils along with DOC. This confirms the hypothesis that complexation with DOC is primarily responsible for the mobility of these metals. Both acid dissolution and organic complexation are important in the mobilization of Al. For Fe, anoxic release from wetlands appears important as well. The export of Pb-DOC complexes from wetlands can cause significant loadings to downstream lakes and has implications for ^{210}Pb dating of both lakes and wetlands. Conversely, there is little correlation of Cd, Zn and Mn with DOC, suggesting that other factors (e.g., acid dissolution) are more important.

INTRODUCTION

Metals in the environment can be brought into aqueous solution by several different processes. These include: proton induced desorption or dissolution of hydroxides at equilibrium (e.g., Al, Mn), the reductive dissolution of hydroxides (e.g., Fe, Mn), strong complexation or chelation with dissolved organic carbon (DOC) (e.g., Pb, Fe, Al) and mineralization of organic matter. Conversely, the loss of metals from solution can be explained by oxidation or precipitation of metal hydroxides, adsorption onto solids and vegetative uptake, precipitation of dissolved DOC-metal complexes. As will be shown, metals that bind tightly to humic substances in "inner sphere", covalent complexes or chelates (e.g., Cu, Fe, Al; Gamble et al. 1970) tend to follow the same pattern of transport as DOC. They accumulate where humic substances accumulate and migrate when humic substances migrate. Some metals generally follow this pattern but are also influenced by redox processes (e.g., Fe) and some by pH induced dissolution of hydroxides (e.g., Al). Other metals appear to behave more independently of DOC (e.g., Cd, Zn and Mn), probably because of their weak "outer sphere", electrostatic bonds to humic substances (Gamble et al. 1976).

As reviews of the literature are readily available (e.g., Kramer and Duinker (eds.) 1984; Campbell et al. 1985; LaZerte 1986; Bergkvist et al. 1989; and Nelson and Campbell 1991), I will merely show here that Pb, Cu and Fe behave as predicted in the dilute waters of the Precambrian Shield in Canada (they closely follow patterns of DOC mobilization) and that Cd, Zn and Mn are not so tightly correlated, if at all, with DOC. Metal concentrations and budgets for two important sites of organic carbon cycling on the Precambrian Shield will be considered:

i) well-drained, usually oxic, *upland* forest soils with living plant, litter and organic soil layers on top of mineral soils or bedrock, and

ii) mineraltrophic, frequently anoxic, *wetland* soils with living plant, litter and organic soil layers on top of organic peat.

The correlation of metal concentrations with DOC is not necessarily an indication of strong "inner sphere" complexation by DOC. Because of the intense microbial mineralization of organic matter, upland organic and wetland soils that produce high quantities of DOC can also produce high concentrations of many ions, especially nutrients such as K, NO_3^-, Mn and Zn. Depending upon the cation, both strong "inner sphere" and weak "outer sphere" complexes with organic anions can form, assisting the transport of these cations in solution. Consequently the field evidence presented here has to be evaluated in concert with more detailed experimental and laboratory studies.

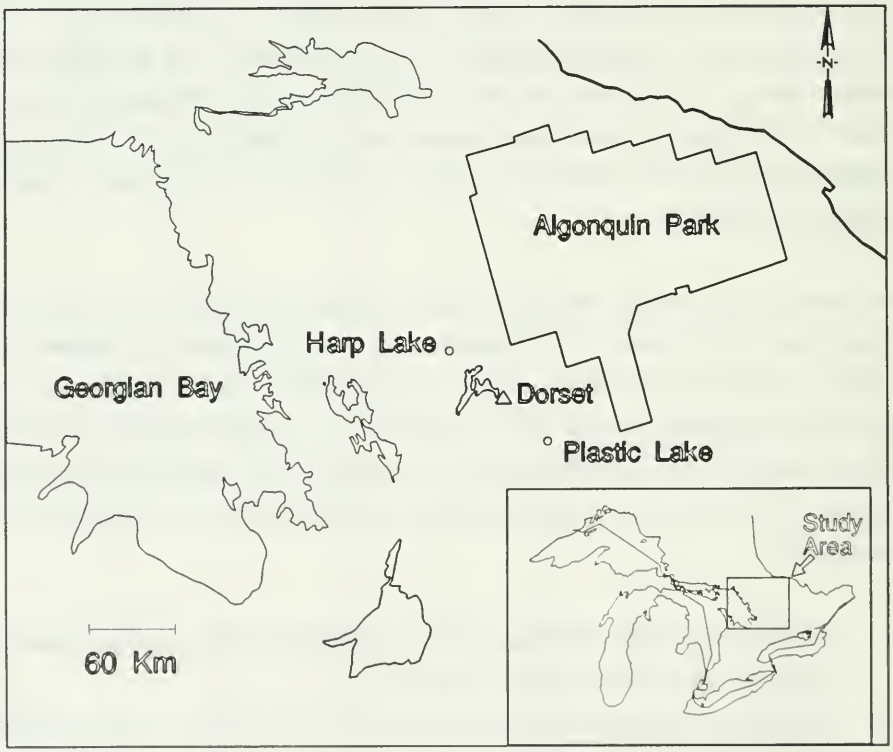

Figure 1

SITES AND METHODS

Ten streams have been sampled and analyzed weekly for trace metals as described in LaZerte et al. (1989). Seven of the streams are in the Harp Lake catchment in the Muskoka-liburton region of Central Ontario while the remainder are in the Plastic Lake catchment (figure 1). The interior of the three largest basins draining into Plastic Lake are dominated by conifer swamps, of which the Plastic 1 (PC1) swamp and sub-catchment (figure 2) are the largest. The upland soils of the PC1 catchment are sandy, shallow (~0.5m) podzols underlain by granites (Lozano 1987; Kirkwood and Nesbitt 1991) and the upland forest cover is dominated by *Pinus strobus*, *Tsuga canadensis* and *Acer rubrum*. The conifer swamp soils are peaty, organic mucks dominated by *Thuja occidentalis* and *Picea mariana* with *Sphagnum sp.* as the dominant ground cover (Lozano and Parton 1987). The Harp Lake catchments are more varied, some with deeper tills, more organic podzolic soils, deeper groundwater reservoirs, extensive wetland coverage and/or forests dominated by *Acer saccharum* (Lozano 1987; Lozano and Parton 1987).

Of the sub-basin areas that drain into the Plastic PC1 swamp, PC1-08 is unique in that it has a fairly long, steadily descending reach. As a consequence, the weir at PC1-08 discharges the greatest amount over the longest period of time; the other swamp surface inputs are very ephemeral. In this talk, I use PC1-08 chemistry and areally pro-rated discharges to estimate all surface water loadings to the swamp. The outflow from the PC1 conifer swamp is monitored at the PC1 weir located about 50 m downstream from a well defined bedrock lip which controls the water level of the swamp.

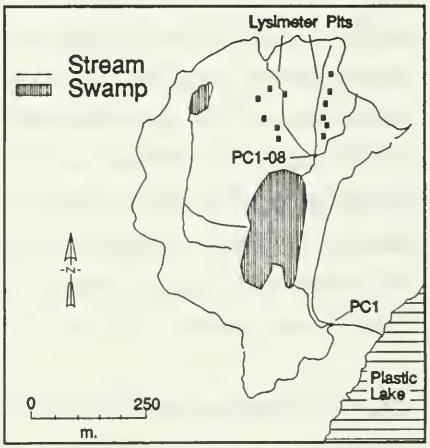

Figure 2

The V-notch weirs at PC1 and PC1-08 are established on a bedrock base with little evidence of leakage. The notches are heated to eliminate ice buildup and provide year-round operation. The stage/discharge relations of the weirs are individually calibrated using Pygmy meters in standard reaches (high flow) or buckets (low flow). The stage is continuously monitored in an isolated, heated stilling well using a float connected to a Leopold-Stevens A71 recorder. The strip charts are digitized and discharge estimated on a daily basis.

A teflon coated wet-only deposition collector located within the Plastic Lake catchment provides precipitation chemistry (LaZerte et al. 1989) of trace metals for the Plastic Lake budgets. A 0.25m^2 teflon coated bulk collector is used for Al, Fe and Mn. Dry deposition of metals is not monitored, but literature values suggest that anything from 0 to 100% of wet-deposition values might be appropriate, with <10% being more likely for Pb (Urban et al. 1990).

Both alundum tension (Neary and Tomassini 1985) and plexiglas zero-tension lysimeters are used to collect soil water leachates just below the organic horizon (LFH) and below the deepest mineral Bf2 horizon (approx. 40-80 cm) from 12 soil pits in the upland soils of the PC-1 catchment. The pits are in the Plastic PC1-08 catchment or directly adjacent to it. Analyses from all twelve pits are averaged on a daily basis by horizon (LFH or Bf2) for interpretation. Flux estimates through the soil horizons assume that all evapotranspiration occurs in the organic LFH layer and canopy, none in the mineral soil. As more than 90% of the roots in these systems occur in the organic soil layers (LaZerte, unpubl. results) , this approximation appears to be reasonable.

Chemical collections were obtained more frequently during high flow periods (twice weekly in spring and fall) than during low flow periods (once weekly when flowing); for the budgets, linear interpolation was used to estimate the chemistry on days between sample collection. Dissolved organic carbon is measured by persulphate digestion preceded and followed by inorganic carbon analysis (OME 1983). Collection procedures and total metal analyses for

precipitation and surface waters were performed as described in LaZerte et al. (1989). For lysimeter soilwater samples, inductively coupled plasma-mass spectroscopy was used for analysis. Aluminum speciation was estimated with the catechol violet / anion exchange method (LaZerte et al. 1988). Rigorous field blank and sample handling protocols were in place (LaZerte et al. 1989), and all data presented here is both significantly and substantially greater than the field blanks.

RESULTS AND DISCUSSION

DOC Relationships

The median concentration of Pb, Cu, Fe and organic Al at twelve sites over a two to five year period is plotted against the median DOC concentration in figure 3. The sites include seven streams from Harp Lake and three from Plastic Lake catchments including the lake outflows, as well as the two average upland lysimeter stations at Plastic Lake catchment (organic LFH and mineral Bf2). A general linear relationship (on a log-log scale) exists for these metals which supports the hypothesis that strong complexation with DOC is their major mechanism of mobilization. If total Al (inorganic + organic) was plotted, little relationship would be found because Al is mobilized both by strong DOC complexation and by acid leaching of Al hydroxides (e.g., LaZerte 1989). The highest DOC point is from upland, oxic soil organic leachates (LFH layer) whereas the mid-range DOC points are from wetland, often anoxic sources. The relatively high Fe levels at the wetland sites compared to the upland site is the result of net anoxic release in the wetlands, as will be shown in the swamp budget below.

Conversely, there is little relationship between Cd, Zn, Mn and inorganic Al and DOC (figure 4). The four lowest Zn values (0.1 ug/L) are actually below the detection limit of our current methods. The organic soil sites (LFH) are high for Cd, Zn and Mn (as well as Pb shown earlier). The two sites with the highest inorganic Al and low DOC levels drain acid, mineral soils in Plastic Lake catchment. The two high Zn, low DOC sites are the

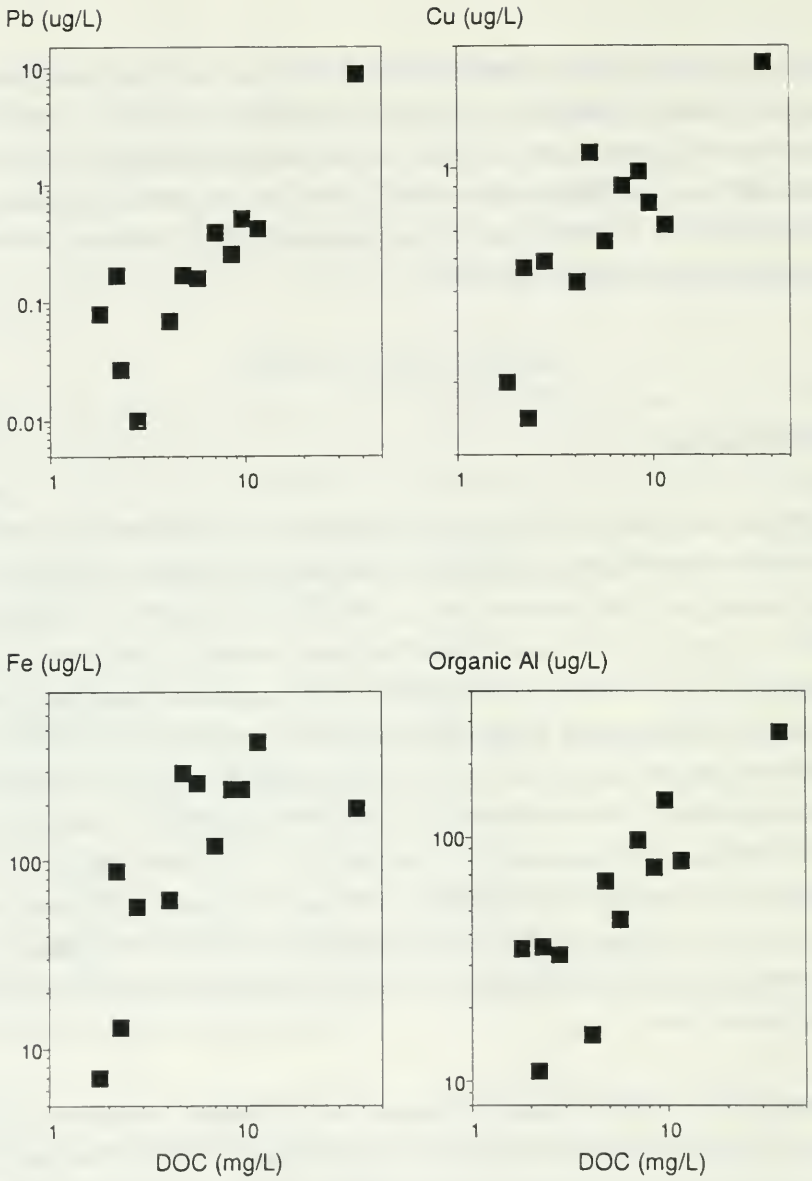
Pb (ug/L)
10
1
0.1
0.01
1
10
Cu (ug/L)
1
1
10
Fe (ug/L)
100
10
1
10
DOC (mg/L)
Organic Al (ug/L)
100
10
1
10
DOC (mg/L)

Figure 3

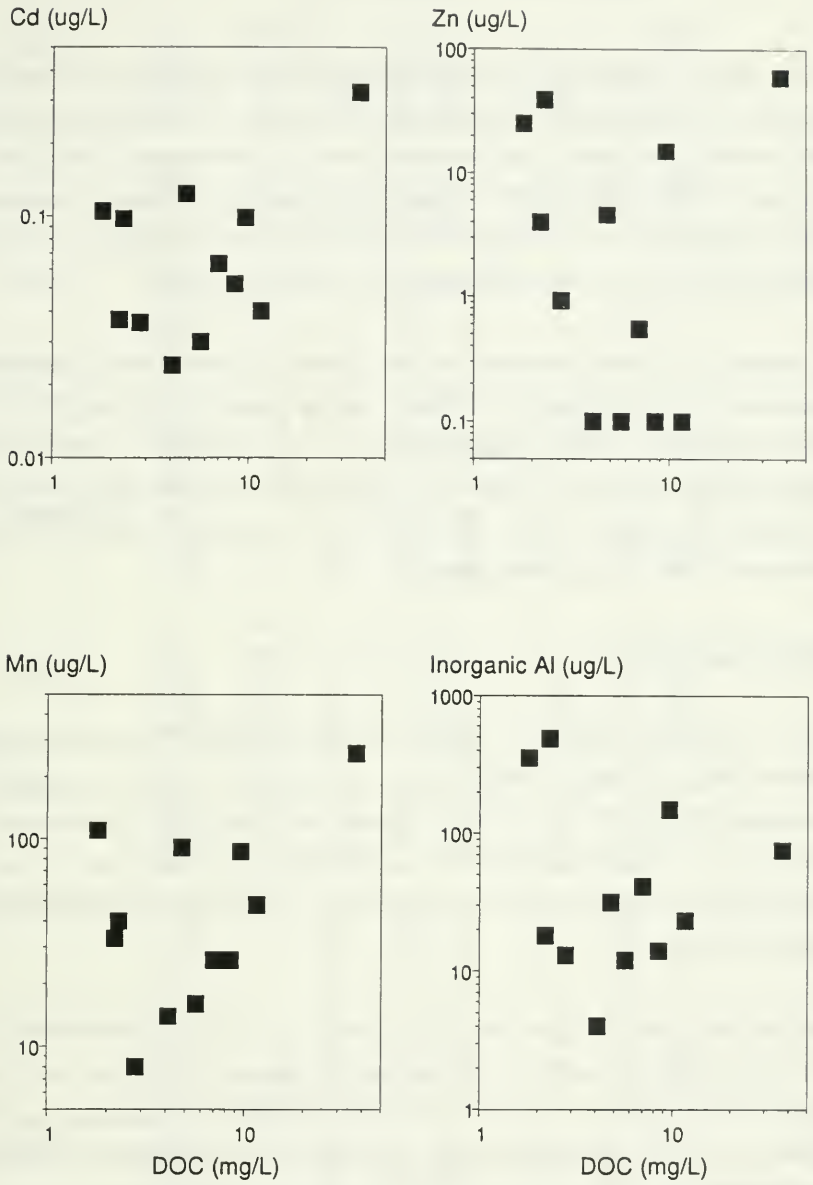
Cd (ug/L)
0.1
0.01
1
10
Zn (ug/L)
100
10
1
0.1
1
10
Mn (ug/L)
100
10
1
10
DOC (mg/L)
Inorganic Al (ug/L)
1000
100
10
1
1
10
DOC (mg/L)

Figure 4

same. In general then, other processes seem to be more important in controlling the concentrations of these metals. Concentrations of inorganic Al are usually found to be in equilibrium with some form of Al tri-hydroxide when the water comes from mineral soils and is low in DOC (LaZerte 1989). High DOC, organic soil and wetland solutions are usually undersaturated and it is thought their inorganic Al concentrations are controlled by the organically bound Al in the solid phase (e.g., Cronan et al. 1986).

In contrast to Fe, the Mn concentrations do not suggest that anoxic wetlands are important contributors. This is confirmed by the swamp budget (below) and is in agreement with LaZerte and Burling's (1990) argument that the pH related solubility of Feitknechtite or Hausmannite mineral phases controls Mn concentrations in oxic, low DOC surface waters on the Precambrian Shield but that high DOC swamp waters (oxic or anoxic) are usually undersaturated with respect to these phases.

Plastic Swamp Budgets

In Table 1, "Total In" = "Precip" + "Runoff" and, where available, four annual budgets (1 September 1986 to 31 August 1990) are presented separately. There is a net export of approximately 37 g of DOC per m^2 of PC1 swamp surface per year. There is also a net export of Pb, Cu, Fe and Organic Al (1.4, 1.3, 620, 361 mg/m^2 respectively). The major input of Pb is direct deposition onto the swamp surface; direct deposition is also relatively important for Cu and Fe.

While it may be argued that historically high deposition loadings of Pb to the swamp (e.g., Urban et al. 1991) could account for the current high net export, the same could not be argued for Fe. An internal source of Fe, probably via diffusion up from a deep, anoxic weathering zone in the glacial till below the swamp must be postulated. A similar Fe pattern has been observed in dystrophic lakes by Nurnberg and Dillon (pers. comm.): the greater the DOC content of the lake, the greater the proportion of internal load of reduced Fe from the anoxic hypolimnia that is exported. Anoxic weathering of primary minerals,

		PC1 Swamp Budgets				PC1 Upland Budgets		
	Year	Precip	Runoff	Total In	Output	LFH	Bf2	PC1-08
DOC (g/m2)	86/87	0.00	7.01	7.01	42.75	9.15	1.06	0.79
	87/88	0.00	9.70	9.70	36.85	14.68	1.29	1.10
	88/89	0.00	10.56	10.56	49.53	20.51	1.51	1.19
	89/90	0.00	9.50	9.50	56.53	15.30	1.22	1.07
	Ave	0.00	9.19	9.19	46.41	14.91	1.27	1.04
Pb (mg/m2)	86/87	NA	NA	NA	NA	NA	NA	NA
	87/88	2.08	0.31	2.39	3.56	NA	NA	0.03
	88/89	1.76	0.66	2.42	3.72	4.29	0.03	0.07
	89/90	1.67	0.46	2.13	3.89	4.83	0.19	0.05
	Ave	1.83	0.48	2.31	3.72	4.56	0.11	0.05
Cu (mg/m2)	86/87	NA	NA	NA	NA	NA	NA	NA
	87/88	0.9	1.6	2.5	3.1	NA	NA	0.2
	88/89	0.8	2.2	3.0	4.0	0.6	0.1	0.2
	89/90	0.8	1.3	2.1	4.4	1.0	0.3	0.1
	Ave	0.9	1.7	2.5	3.8	0.8	0.2	0.2
Fe (mg/m2)	86/87	29	177	206	1081	64	69	20
	87/88	41	36	77	441	82	48	4
	88/89	21	20	41	681	122	14	2
	89/90	24	30	54	651	83	7	3
	Ave	29	66	95	714	88	34	7
Al Organic (mg/m2)	86/87	0	147	147	468	221	15	17
	87/88	0	156	156	410	112	16	18
	88/89	0	253	253	658	187	30	29
	89/90	0	173	173	636	93	14	20
	Ave	0	182	182	543	153	19	21

	Year	Precip	Runoff	Total In	Output	LFH	Bf2	PC1-08
Cd (mg/m2)	86/87	NA	NA	NA	NA	NA	NA	NA
	87/88	0.18	0.76	0.94	0.72	NA	NA	0.09
	88/89	0.08	0.75	0.83	0.92	NA	NA	0.08
	89/90	0.12	0.37	0.49	0.44	0.18	0.08	0.04
	Ave	0.13	0.62	0.75	0.69	0.18	0.08	0.07
Zn (mg/m2)	86/87	NA	NA	NA	NA	NA	NA	NA
	87/88	3	93	96	80	31	22	10
	88/89	3	118	121	77	36	28	13
	89/90	3	145	148	70	32	35	16
	Ave	3	118	121	76	33	28	13
Mn (mg/m2)	86/87	5	507	512	227	22	14	57
	87/88	5	510	515	571	95	28	58
	88/89	4	548	551	508	156	32	62
	89/90	4	531	535	513	107	25	60
	Ave	4	524	528	455	95	25	59
Al Inorganic (mg/m2)	86/87	9	776	785	210	NA	131	88
	87/88	9	1498	1507	545	67	222	169
	88/89	9	1909	1918	460	69	309	216
	89/90	8	1821	1828	589	61	272	206
	Ave	9	1501	1510	451	66	233	169
Al (mg/m2)	86/87	9	1095	1104	1019	428	151	124
	87/88	9	1968	1978	1126	239	295	222
	88/89	9	2376	2385	1390	371	392	268
	89/90	8	2523	2530	1734	219	377	285
	Ave	9	1990	1999	1317	314	304	225

Table 1

diffusion upwards and then complexation with DOC in the oxic surface water could also explain part of the internal source of Pb and Cu. But most of the net export of Pb is probably due to the historical deposition of anthropogenic Pb onto the PC1 swamp and dry deposition is probably not important (see the Upland budget below; Urban et al. 1991). Nonetheless, more detailed studies of dry deposition, within swamp diffusion gradients and deep mineral compositions are required.

The net export of organic Al results from the retention of inorganic Al. There is little apparent change in Cd and Mn concentrations as they pass through the PC1 swamp; however, Zn, like inorganic Al, is somewhat retained (approx. 45 mg/m^2). Both Zn and Al concentrations are elevated in the surrounding upland soil waters because of the anthropogenic acidification, and it is also likely that Zn (like Al) has a some affinity for humic substances which would explain its retention in the swamp.

Plastic Upland Budgets

Approximately 15 g DOC per m^2 of upland soil per year is exported from the upper organic soil horizons (LFH). Less than 9% of this passes the lower mineral soil horizons (Bf2) and less than 7% is exported to the swamp through the PC1-08 weir (Table 1). The concentrations of DOC in runoff from these upland soils is some of the lowest we have measured in local surface waters. There is also a net export of Pb, Fe and Organic Al (2.7, 59, 154 mg/m^2 respectively) from the LFH. Less than 2% of the Pb, 9% of the Fe, and 13% of the organic Al enter the swamp. Cu export from the LFH approximately equals precipitation inputs (0.85 mg/m^2) of which 25% enters the swamp. As with the swamp budgets, it is most likely that the historically high Pb deposition accounts for the current net export of Pb from the LFH. The role of dry deposition, however, requires further study. The loss of all these metals in the mineral soil is most likely the result of their organic forms precipitating or adsorbing to Fe and Al hydroxides.

Both Cd and Mn also show a concentration peak in the LFH followed by a loss in the lower mineral soils. This in itself cannot be used as evidence for strong DOC-metal complexation, especially since other ions such as K show an even more pronounced pattern. More likely these cations are traveling down the soil profile as electrostatically bound "outer-sphere" cations (Gamble 1973; Gamble et al 1976) and then co-precipitating with Fe/Al-DOC or adsorbing onto clays in the lower soil horizons. More detailed study is required to verify this hypothesis. Some Mn reappears in the PC1-08 stream bed perhaps because of marginally reducing conditions. Inorganic Al is released in the mineral soil horizons but then some is lost before the swamp as the pH of the ground water solution rises (LaZerte 1989). It also appears that Zn is transported further down the soil profile than Cd or Mn, perhaps because of greater solubility than Cd and Mn in these acidified soils.

Further Studies

In addition to the studies reported here, Mierle and Ingram (1991) have reported a strong correlation between Hg and colour in these waters. They conclude that "humic matter controls the solubility and watershed export of Hg deposited in precipitation". Whether this correlation is the result of strong DOC complexation with Hg or whether methyl-Hg production is enhanced in high DOC waters requires further study. Mierle has also shown that because DOC export is directly related to percentage wetland area in Precambrian Shield catchments, so Hg export is also highly correlated to percentage wetland area (Mierle, pers. comm.).

Mierle (1990) has also estimated the percentage of total Hg load to Harp Lake that comes from the surrounding catchment as 43%, with the remainder entering as direct deposition. Similar calculations for Pb loading to Plastic Lake show that 20-26% of the lake's loading can come from surface runoff. Higher values would be expected for lakes with higher percentage wetland in their catchment. However, for the purposes of dating sediment cores, it is usually assumed that external loading of Pb and ^{210}Pb is negligible to lakes. Conversely it is also assumed, when examining historical trends in metal deposition from swamp peat

profiles, that the lead directly deposited on peat is not mobilized. Clearly this cannot be the case for Plastic Lake swamp where more Pb is leaving than entering, and it is becoming increasingly clear elsewhere that neither assumption is correct (Urban et al. 1991).

CONCLUSIONS

In general, Pb, Fe, Al and Cu all behave as if covalent "inner sphere" complexation with DOC is the primary factor determining their movement on the Precambrian Shield in Canada. Reduction and dissolution of Fe^{2+} is also important, especially when DOC is available in adjacent oxic zones (e.g., wetlands and dystrophic lakes). For Al, acid leaching is as important as DOC complexation in acidified catchments. For Cd, Zn and Mn, acid leaching appears to be the most important process although electrostatic "outer sphere" complexation with DOC may also be relevant.

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